

Infrared Absorption Spectra of Five Halomethanes

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The infrared absorption spectra of five halomethanes, bromodifluoromethane, dibromodifluoromethane, bromochlorodifluoromethane, bromotrifluoromethane, and iodotrifluoromethane have been studied from 2 to 38 microns. Fundamental, combination, overtone, and difference bands have been identified. Many unobserved fundamentals have been predicted by comparisons with related molecules and with Raman spectra. The fundamentals have been classified as to the type of motion and the principal atom involved. Four tables are included to show the relationships among the fundamentals of the molecules compared.

1. Introduction

The infrared spectra of bromodifluoromethane, dibromodifluoromethane, bromochlorodifluoromethane, bromotrifluoromethane, and iodotrifluoromethane have been measured from 2 to 38 μ . The purpose of the measurements was to identify the fundamentals and to classify them as to their modes of vibration. The resulting classification allows a comparison of the vibrations of these molecules with other related substituted methanes studied by other investigators [1].¹ Recently Decius subjected many methane derivatives to a normal coordinate treatment and quantitatively verified the experimental assignments [2]. Plyler and Benedict extended the calculations of Decius and were able to check some of the assignments of the molecules they studied [3]. In addition, the Raman spectra of the molecules have been investigated [4].

2. Instrumentation

A double-beam Perkin-Elmer model 21 spectrophotometer measured the compounds from 2 to 15 μ , and a single-beam Perkin-Elmer spectrometer extended the measurements from 15 to 38 μ . A KBr prism was used from 15 to 23 μ and a TlBr-I prism from 23 to 38 μ .

For most of the measurements from 2 to 23 μ , a 5-cm gas cell with pressures of 1 atm or less was used. In order to detect some of the weak absorption bands, two cells of 40- and 130-cm lengths were employed. These two cells could not be evacuated. They were filled by flowing gases through them.

The five compounds were supplied by R. C. McHarness of the Jackson Laboratories. Tests made by the Bureau's Mass Spectrometry Section indicated minute traces of foreign halogenated-methanes in four of the compounds. Only CBr_2F_2 had impurities in slight excess of 3 percent. These impurities were not observed in the CBr_2F_2 spectrum, probably because they were masked by the strong absorption bands of the molecule.

3. Results

Figure 1 shows the absorption spectra of CHBrF_2 , CBr_2F_2 , and BrClF_2 in the region from 2 to 15 μ . The cell length was 5 cm for all measurements. The

pressure used is indicated on the graph. It is seen that pressures as low as 0.01 cm of Hg were necessary to resolve the structures of the strongest bands. In some cases, it is possible to tell from the graph whether the bands have P, Q, and R, or only P and R branches.

Figure 2 shows the absorption spectra of CBrF_3 and ClF_3 from 2 to 15 μ . The pressures of the gases are indicated next to the respective traces. The cell length employed was also 5 cm. The curves in figures 1 and 2 are traces from the original record obtained from the double-beam spectrophotometer. These graphs have not been corrected for surface reflection of the cells or for stray radiation in the instrument. However, a reflection filter was used beyond 9.2 μ , and as a consequence, the stray radiation did not exceed 5 percent at any wavelength.

Figure 3 shows the infrared absorption spectra of the five compounds in the region from 14 to 36 μ . These measurements were extended to 38 μ , but no bands were observed beyond 36 μ . These compounds were measured in the gaseous state, using cells of 5, 40, and 130 cm in length. The pressures, where measureable, are indicated on the graph. Attempts were made to examine the spectra of these molecules as a liquid because many of the fundamentals did not appear in the gaseous state. However, due to the high volatility of all the compounds at room temperature, only CBr_2F_2 could be measured in this manner. A liquid cell with a thickness 1.5 mm was used for these measurements. The portion of the curves drawn in broken lines indicates that weak absorption bands could not be observed because of atmospheric bands. Table 1 gives a list of wavelengths of all the bands that appear in the infrared. In addition, there are listed bands that do not appear either because their intensity is too weak or because they fall outside the wavelength region studied. These frequencies are taken either from the Raman spectra or from overtone and combination bands. Some of these frequencies have also been predicted by comparison with analogous halomethanes. When a band has been sufficiently resolved by the prism spectrometers, the P, Q, and R, or P and R branches have been listed separately. The intensities are indicated adjacent to the respective band, and these are denoted by abbreviations of very weak, weak, medium, strong, and very strong. The fundamentals have been designated by the numbering system proposed by Plyler and Benedict [3]. Using

¹ Figures in brackets indicate the literature references at the end of this paper.

this notation, it is possible to see the regularities that exist among related molecules of different symmetry. Another way of denoting the fundamentals, which was also used, is to characterize them by the molecular motion involved. In this system, ν_x represents the stretching vibration between the central carbon and the X atoms, and δ_x signifies the bending of the X atom against the rest of the molecule.

The number of fundamentals expected in these molecules can be predicted, as is well known, from symmetry considerations. The five compounds can be put into three point groups. CBrClF_2 and CHBrF_2 have only one plane of symmetry (the CBrCl and CHBr plane, respectively), and thus belong to the point group C_s , whereas CBr_2F_2 has two symmetry planes, placing it in C_{2v} . The molecules CBrF_3 and ClF_3 have a threefold axis of sym-

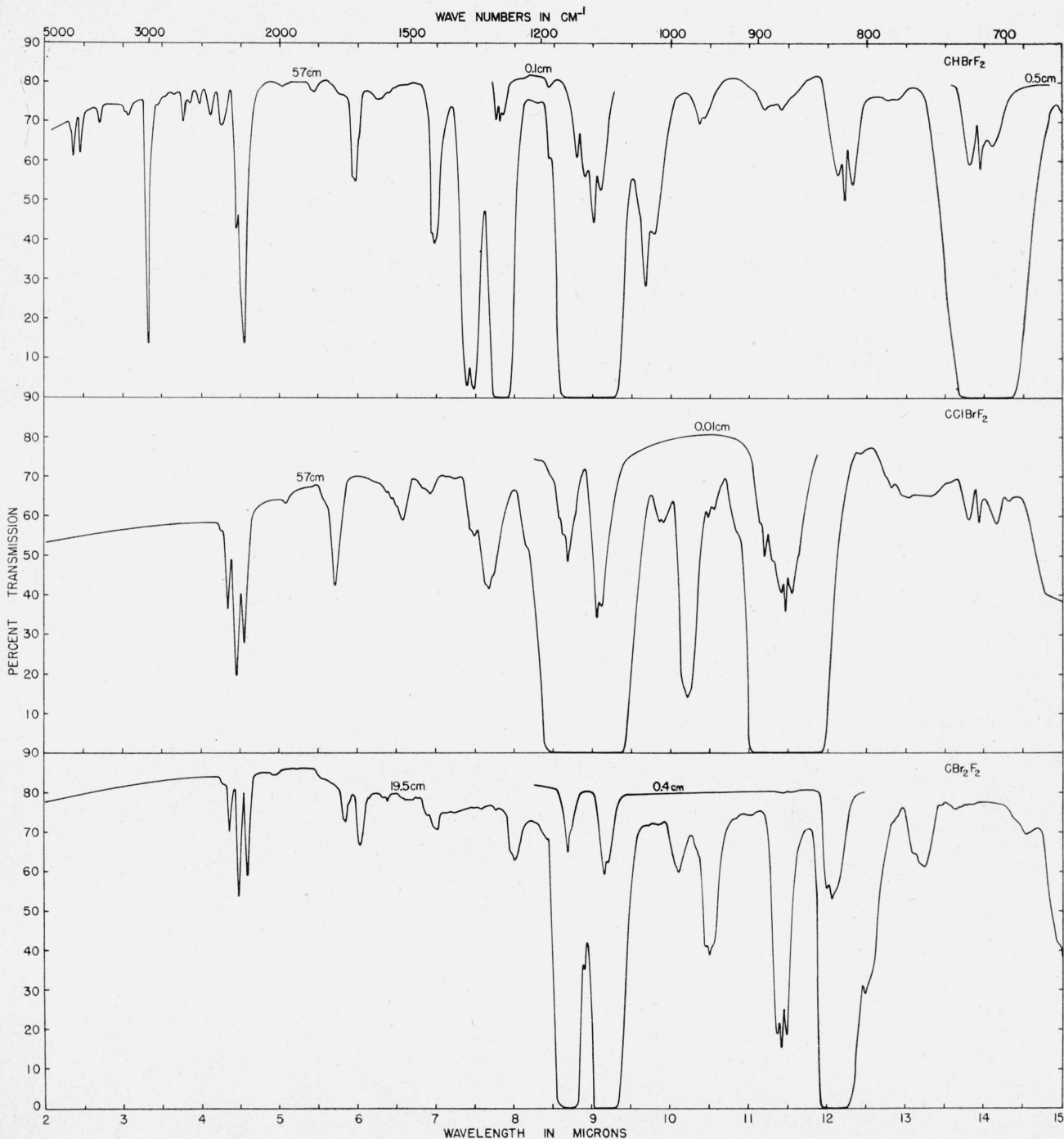


FIGURE 1. Infrared absorption spectra of bromodifluoro-methane, bromochlorodifluoromethane, dibromodifluoromethane from 2 to 15 μ .

TABLE 1. Classification of the infrared bands of bromodifluoromethane, bromochlorodifluoromethane, dibromodifluoromethane, bromotrifluoromethane, and iodotrifluoromethane

λ	ν	I	Assignments
CHBrF ₂			
μ	Cm^{-1}		
3.33	3003	S	ω_1
7.40 R	1351	-----	ω_5
7.44	1344	S	
7.48 P	1337	-----	
7.76 R	1289	-----	
7.81 Q	1280	S	ω_6
7.85 P	1274	-----	
8.81	1135	S	ω_3
8.90 R	1123	-----	
9.02 Q	1108	S	ω_4
9.10 P	1099	-----	
13.82 R	724	-----	
13.93 Q	718	S	ω_7
14.12 P	708	-----	
17.11 R	584	-----	
17.34 Q	577	S	ω_9
17.48 P	572	-----	
31.0	323	VW	ω_5
41.6	^a 240	-----	ω_2
2.36	4237	W	$\omega_6 + \omega_1$
2.45	4080	W	$\omega_3 + \omega_1$
2.69	3716	VW	$\omega_7 + \omega_1$
3.06	3267	VW	$\omega_2 + \omega_1$
3.76	2659	VW	$2\omega_8$
3.83	2610	VW	$\omega_8 + \omega_6$
3.96	2525	VW	$2\omega_6$
4.10	2438	VW	$\omega_8 + \omega_9$
4.25	2352	VW	$2\omega_3$
4.44	2252	W	$\omega_3 + \omega_9$
4.55	2197	M	$2\omega_9$
5.03	1988	VW	$\omega_7 + \omega_6$
5.19	1926	W	$\omega_8 + \omega_4$
5.97	1675	W	$\omega_4 + \omega_9, \omega_5 + \omega_8$
6.25	1600	VW	$\omega_2 + \omega_5, \omega_5 + \omega_6$
6.97	1434	W	$2\omega_7$
8.44	1185	W	$2\omega_4$
9.68	1033	M	$\omega_5 + \omega_7$
10.37	964	VW	$\omega_2 + \omega_7$
11.20	893	VW	$3\omega_4 + \omega_5$
11.42	875	VW	
12.14 R	824	-----	
12.22 Q	818	W	$\omega_2 + \omega_4$
12.34 P	810	-----	
15.52	644	M	$2\omega_5$
CBr ₂ F ₂			
9.15 R	1093	-----	ω_1
9.19	1088	-----	ω_8
9.21 P	1086	-----	ω_6
8.69 Q	1150	VS	ω_5
12.06 Q	829	VS	
16.03 R	624	-----	ω_3
16.10	621	VS	
16.18 P	618	-----	ω_4
29.4	^b 340	-----	ω_9
27.2	^b 367	-----	ω_7
30.2	^c 331	VW	ω_5
35.5	^b 282	-----	ω_2
60.6	^b 165	-----	$2\omega_8$
4.37	2288	W	$\omega_8 + \omega_1$
4.50	2222	W	$2\omega_1$
4.60	2173	W	$\omega_1 + \omega_3$
5.85	1709	VW	$2\omega_6$
6.05	1652	VW	$\omega_6 + \omega_3$
6.90	1449	VW	$\omega_7 + \omega_1$
7.00	1428	VW	$2\omega_3$
8.00	1250	W	$\omega_6 + \omega_5$
8.91	1122	W	$3\omega_7, \omega_2 + \omega_6$
10.10	990	-----	$\omega_7 + \omega_3$
10.45 R	957	-----	
10.50 Q	952	M	
10.55 P	948	-----	$\omega_5 + \omega_3$
10.96	912	VW	
11.37 R	880	-----	$\omega_8 - \omega_5$
11.43 Q	875	M	
11.49 P	870	-----	
12.49	800	-----	$\omega_3 + \omega_2$
13.19	758	W	$\omega_1 - \omega_1$
13.75	727	VW	$\omega_1 - \omega_9$
14.54	688	VW	$2\omega_4$
15.10	662	M	$2\omega_7$
20.90	478	VW	$\omega_6 - \omega_7, \omega_2 + \omega_7$

See footnotes at end of table.

TABLE 1. Classification of the infrared bands of bromodifluoromethane, bromochlorodifluoromethane, dibromodifluoromethane, bromotrifluoromethane, and iodotrifluoromethane—Continued

λ	ν	I	Assignments
CBrClF ₂			
9.07	1102	VS	ω_1
8.69	1150	VS	ω_8
11.42 R	876	-----	
11.47 Q	872	VS	ω_6
11.55 P	866	-----	
15.48	648	VS	ω_3
25.0	^a 400	-----	ω_4
26.3	^a 380	-----	ω_7
22.7	440	VW	ω_9
33.3	^a 300	-----	ω_5
50.0	^a 200	-----	ω_2
4.35	2298	W	$2\omega_8$
4.46	2241	M	$\omega_8 + \omega_1$
4.56	2192	W	$2\omega_1$
5.09	1964	VW	$\omega_1 + \omega_6$
5.73	1745	M	$\omega_1 + \omega_3$
6.58	1519	W	$\omega_6 + \omega_3$
6.93	1443	VW	$\omega_8 + \omega_5$
7.49	1335	VW	$\omega_8 + \omega_2$
7.68	1302	M	$\omega_6 + \omega_9, 2\omega_3, \omega_1 + \omega_2$
9.90	1110	W	$\omega_3 + \omega_9$
10.23	977	M	$\omega_7 + \omega_3$
10.49	953	VW	$\omega_3 + \omega_5$
12.83	779	VW	$\omega_1 - \omega_5$
13.82 R	724	-----	
13.95 Q	716	W	$\omega_4 + \omega_5$
14.17 P	706	-----	
CBrF ₃			
9.21	1085	S	ω_1
8.29	1206	VS	ω_8
13.04 R	767	-----	
13.14 Q	761	S	ω_3
13.26 P	754	-----	
28.7	348	VW	ω_4
18.17	550	W	ω_7
55.5	^b 180	-----	ω_{25}
4.18	2392	M	$2\omega_8$
4.38	2282	M	$\omega_8 + \omega_1$
4.62	2164	VW	$2\omega_1$
5.10	1960	W	$\omega_8 + \omega_3$
5.30	1886	W	$2\omega_7 + \omega_3$
5.42	1844	W	$\omega_1 + \omega_3$
5.70	1754	W	$\omega_8 + \omega_7$
6.15	1626	W	$\omega_1 + \omega_7$
6.64	1507	W	$2\omega_3$
6.80	1470	W	$2\omega_7 + \omega_4$
7.01	1426	W	$\omega_1 + \omega_4$
7.23	1383	W	$\omega_8 + \omega_{25}$
7.66	1305	M	$\omega_3 + \omega_7$
8.52	1173	M	?
8.92	1121	M	$\omega_3 + \omega_4, 2\omega_7$
10.53	949	VW	$\omega_{25} + \omega_3$
10.92	915	VW	$\omega_1 - \omega_{25}$
11.77	849	W	$\omega_8 - \omega_4$
11.99 P	833	-----	
12.05 Q	830	W	$\omega_8 - \omega_4$
12.11 P	826	-----	
13.68	735	M	$\omega_1 - \omega_4, \omega_{25} + \omega_7$
14.25	700	M	$2\omega_4$
14.50	689	M	?
21.3	470	VW	?
CF ₃ I			
9.26 R	1080	-----	ω_1
9.32 Q	1073	VS	
9.36 P	1068	VS	ω_8
8.44 Q	1186	-----	
13.40 R	746	-----	ω_3
13.50 Q	740	S	
13.61 P	735	-----	
35.2	284	W	ω_4
18.17	550	M	ω_7
61.3	^a 163	-----	ω_{25}
2.86	3495	VW	$2\omega_8 + \omega_1$
2.94	3409	VW	$2\omega_1 + \omega_8$
3.45	2898	VW	$2\omega_8 + \omega_7$
4.10	2438	VW	$\omega_3 + \omega_7 + \omega_{25}$
4.28	2336	W	$2\omega_8$
4.45	2246	M	$\omega_1 + \omega_8$
4.55	2197	VW	$3\omega_3$
4.67	2141	W	$2\omega_1$
4.76	2100	VW	$2\omega_7 + \omega_1$
5.22	1915	W	$\omega_3 + \omega_8$
5.50	1818	VW	$\omega_1 + \omega_3$
5.81	1721	W	$\omega_8 + \omega_7$

TABLE 1. Classification of the infrared bands of bromodifluoromethane, bromochlorodifluoromethane, dibromodifluoromethane, bromotrifluoromethane, and iodotrifluoromethane—Continued

λ	ν	I	Assignments
CF ₃ I—Continued			
6.23	1605	W	$\omega_1 + \omega_{79}$
6.93	1443	VW	$2\omega_3, \omega_4 + \omega_{68}$
7.52	1329	W	$\omega_{88} + \omega_{25}$
8.02	1246	M	$\omega_1 + \omega_{25}$
8.97 Q	1114	W	$2\omega_{79}$
9.70 R	1031	---	---
9.75 Q	1025	M	$\omega_3 + \omega_4$
9.80 P	1020	M	---
10.91	916	VW	$\omega_1 - \omega_{25}, \omega_{25} - \omega_3$
12.18	820	W	$\omega_4 + \omega_{79}$
12.87	776	VW	$\omega_1 - \omega_4$
14.05	711	VW	$\omega_{25} + \omega_{79}$
22.30	448	W	$\omega_4 + \omega_{15}$

a Predicted from combination and overtone bands.

b Raman value.

c Liquid.

metry and three planes of symmetry. Therefore they belong to the point group C_{3v} . Molecules in the point group C_{3v} have six different active fundamentals, whereas those in C_{2v} and C_s have nine, one of which ω_5 , is theoretically inactive in the infrared, but which is actually found in this type of molecule.

Six methods were used to identify and classify the fundamental vibrations of the five halomethanes, as follows: (1) comparison with available Raman spectra; (2) comparison with the calculated values of Stepanov [5]; (3) comparison with similar molecules, that is, isotope effect; (4) calculation based on overtone and combination bands; (5) intensity considerations; and (6) consideration of band envelopes.

In table 2 are shown the nine infrared fundamental frequencies of $CHBrF_2$. These are compared with the calculated values of Stepanov and with the assigned fundamentals of $CHClF_2$. Of eight fundamentals found in the infrared, seven give rise to strong bands. Stepanov estimates that his calculated values are accurate to within 30 to 50 cm^{-1} . Six of the nine fundamentals fall within this accuracy. The classification of $CHBrF_2$, as to the modes of motion and the main atom involved, is based on the assignments of the related molecule $CHClF_2$. Six of the fundamentals should have almost the same value for the two molecules, as they involve primarily the motions of the same atoms. The other three vibrations, ν_{Br} , δ_{BrF} , and δ_{Br} , should all occur at smaller wave numbers than the corresponding vibration ν_{Cl} , δ_{FCl} , and δ_{Cl} . This is the case for the

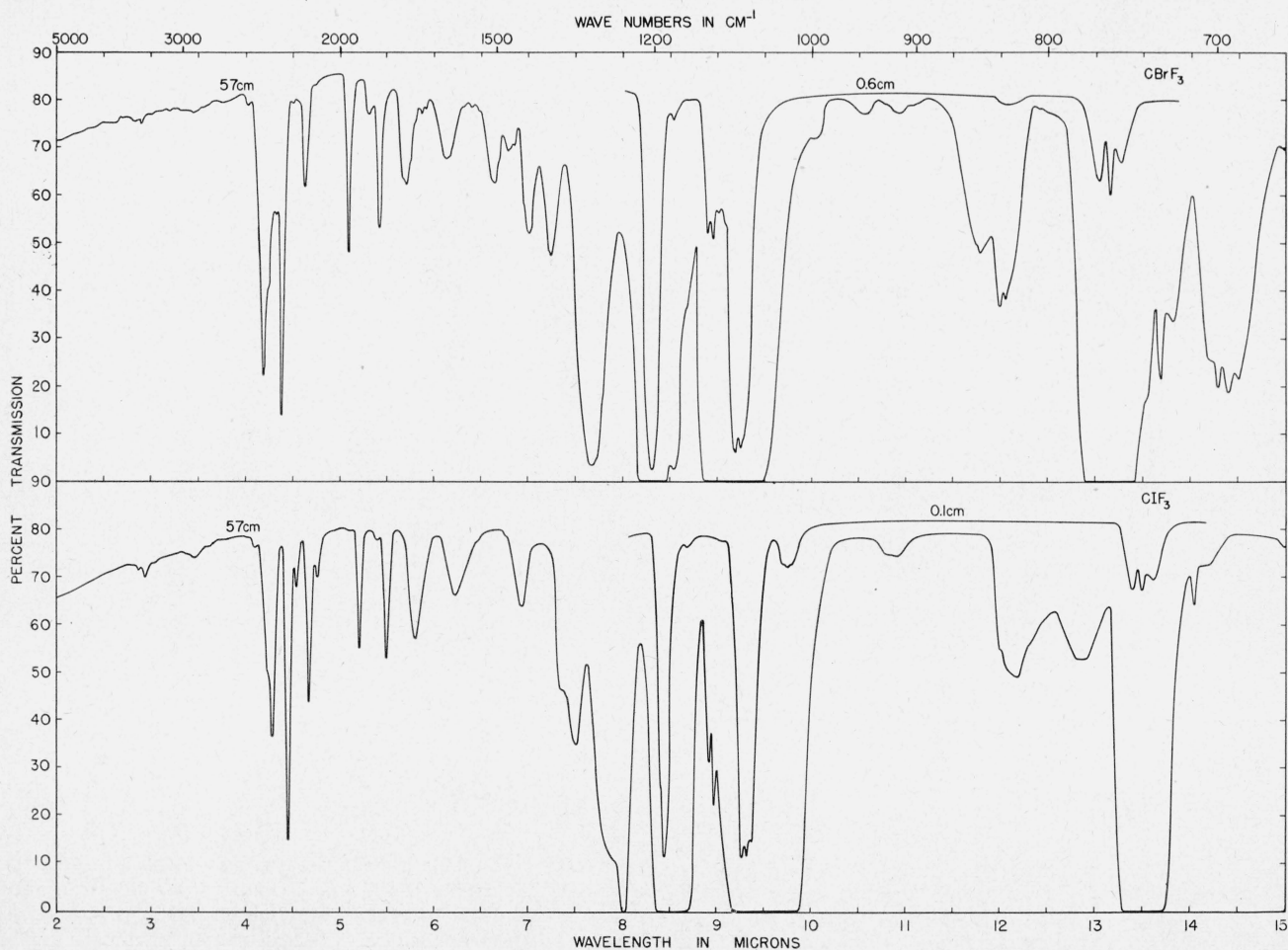


FIGURE 2. Absorption spectra of bromotrifluoromethane and iodotrifluoromethane from 2 to 15 μ .

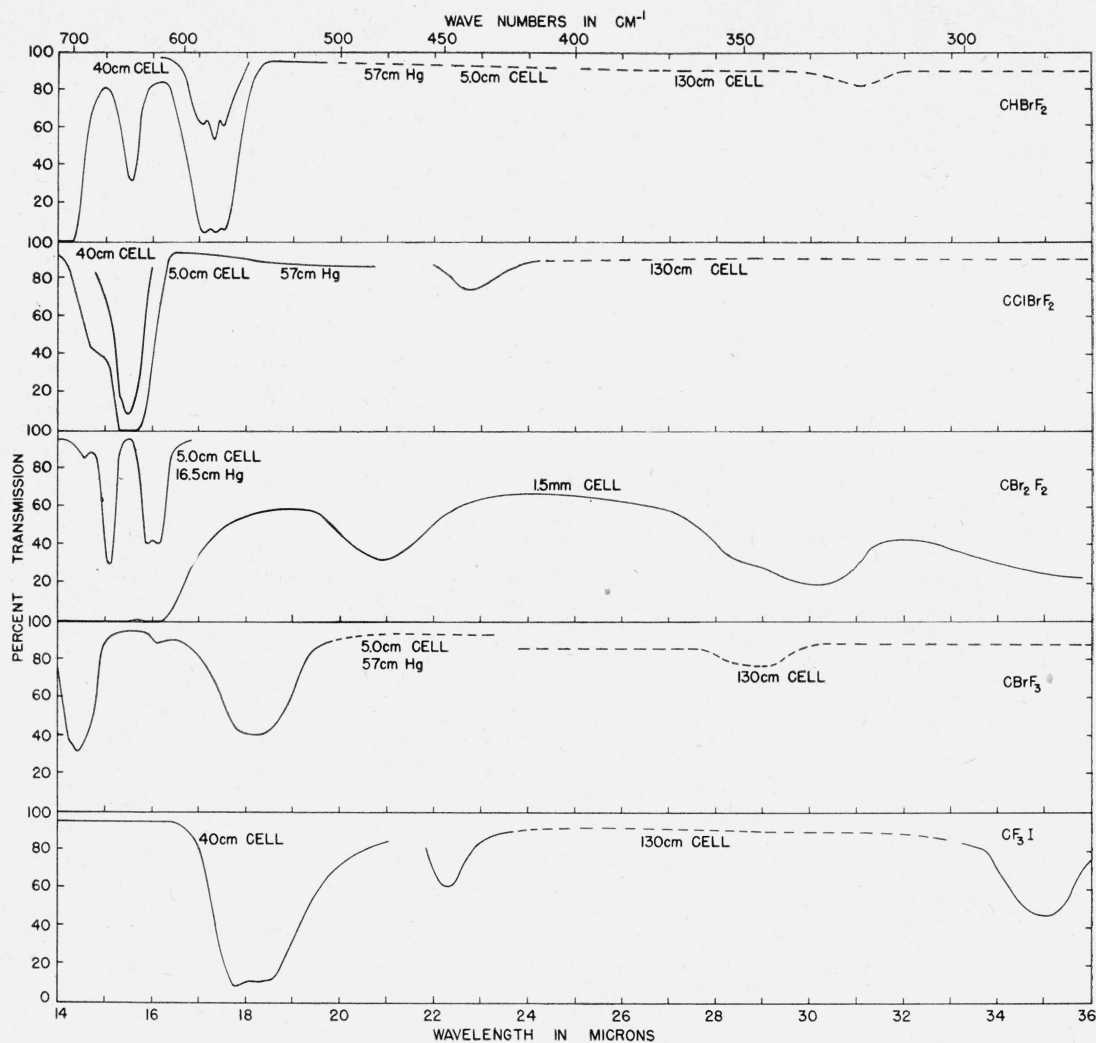


FIGURE 3. Infrared absorption spectra of bromodifluoromethane, bromochlorodifluoromethane, dibromodifluoromethane, bromotrifluoromethane, and iodotrifluoromethane from 14 to 36 μ .

assignments in table 2. The frequency, 240 cm^{-1} , which was outside the TIBr-I region, was determined from the combination bands. The value 240 cm^{-1} for ω_2 seems more probable for the bending vibration of bromine than the calculated value of the 320 cm^{-1} when related molecules are considered.

TABLE 2. Infrared fundamentals of bromodifluoromethane compared with the fundamentals of chlorodifluoromethane and with the calculated values of Stepanov

Classification	CHClF_2 , infrared gas, ν	CHBrF_2 , infrared gas, ν	CHBrF_2 , calculated, ν
	cm^{-1}	cm^{-1}	cm^{-1}
ω_1	3023, ν_{H}	3003, ν_{H}	3030
ω_8	1347, δ_{H}	1344, δ_{H}	1350
ω_6	1311, δ_{H}	1280, δ_{H}	1300
ω_3	1178, ν_{F_2}	1135, ν_{F_2}	1110
ω_4	595, δ_{F_2}	576, δ_{F_2}	550
ω_7	809, ν_{Cl}	718, ν_{Br}	660
ω_9	1116, ν_{F_A}	1108, ν_{F_A}	1070
ω_5	365, δ_{FCl}	323, δ_{FBr}	380
ω_2	422, δ_{Cl}	^a 240, δ_{Br}	320

^a Predicted from combination and overtone bands.

The six fundamentals of CBrF_3 and CF_3I have been accounted for by a comparison with the calculated values of CBrF_3 of Stepanov and with the fundamental frequencies of the related symmetric top molecule CClF_3 previously studied. Five of the fundamentals of CBrF_3 and CF_3I fall within the spectral region measured. The sixth fundamental, ω_{25} , was determined from the calculated value for CBrF_3 , and for CF_3I it was determined from the combination bands. The ν_{FS} , ν_{FA} , and δ_{FA} vibrations of the three molecules have almost the same frequencies. It is somewhat unusual that the vibrations ν_{Cl} , ν_{Br} , and ν_{I} are almost equal. This effect may be produced by the small C-F distances in these molecules. The intensities of ω_4 and ω_{79} , the δ_{F} for both compounds, are very weak. This appears to be typical of this vibration and is found to occur in similar fluoromethanes. The selection of these two frequencies as fundamentals seems justifiable on the basis of the overtone and combination bands. Table 3 also shows that the effect of replacing a chlorine by

TABLE 3. Comparison of the fundamentals of bromotrifluoromethane and iodotrifluoromethane with the infrared fundamentals of chlorotrifluoromethane and with the calculated fundamentals of Stepanov.

Classification	CClF ₃ , infrared gas, ν	CBrF ₃ , infrared vapor, ν	CBrF ₃ , ^a calculated, ν	CF ₃ I, infrared gas, ν
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
ω_1	1105, ν_{F_8}	1085, ν_{F_8}	950	1073, ν_{F_8}
ω_{68}	1212, ν_{F_8}	1206, ν_{F_8}	1140	1186, ν_{F_8}
ω_3	781, ν_{C1}	761, ν_{Br}	730	740, ν_1
ω_4	470, δ_{F_8}	348, δ_{F_8}	340	284, δ_{F_8}
ω_{79}	563, δ_{F_8}	550, δ_{F_8}	580	550, δ_{F_8}
ω_{25}	356, δ_{C1}	^b 180, δ_{Br}	180	^a 163, δ_1

^a Predicted from combination and difference bands.

^b Calculated value of Stepanov.

a bromine or iodine is to shift the corresponding vibrations to longer wavelengths. Except for δ_{Br} and δ_1 , there is little doubt in the assignments of the fundamentals of these two molecules.

Some difficulty was experienced in the assignment of the fundamentals of the molecule CBr₂F₂ and CBrClF₂. Five fundamentals appear at wave numbers less than 440 cm^{-1} . The intensities of these bands are low. Furthermore, three of the bands, ω_4 , ω_7 , and ω_9 , overlap and could not be resolved. Nevertheless, provisional assignments have been made for CBr₂F₂ and CBrClF₂, based on a comparison with the Raman spectra of Glocker and Leader [6], the calculated values, and also the infrared values of the related halomethane CCl₂F₂. The relationships among the three molecules can be seen from table 4. Five infrared fundamentals for CBr₂F₂ were found, and these check well with the Raman spectra. The bands at 1088, 1150, 829, and 621 cm^{-1} are all very strong, but the band at 331 cm^{-1} measured in the liquid state is very weak. The five frequencies are all smaller in wave number than the five corresponding frequencies of CCl₂F₂, as would be expected. The remaining frequencies ω_4 , ω_9 , ω_5 , and ω_2 were too weak to be determined in the infrared, and consequently the Raman values have been accepted and classified. As the fundamentals ω_4 , ω_7 , and ω_9 overlap, the assignments of these bands are doubtful.

CBrClF₂ can be considered an isotopic molecule of either CBr₂F₂ or CCl₂F₂. Its fundamentals should be intermediate in value. This is seen to be the case for the four strong infrared bands at 1102,

TABLE 4. Comparison of the infrared fundamentals of dibromodifluoromethane and bromochlorodifluoromethane with the infrared values of dichlorodifluoromethane, the Raman values of dibromodifluoromethane, and the calculated values of bromochlorodifluoromethane.

Classification	CBr ₂ F ₂ , infrared gas, ν	CBr ₂ F ₂ , Raman liquid, ν	CBrClF ₂ , infrared gas, ν	CBrClF ₂ , calculated, ν	CCl ₂ F ₂ , infrared gas, ν
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
ω_1	1088, ν_{F_8}	1077	1102, ν_{F_8}	1070	1101, ν_{F_8}
ω_8	1150, ν_{F_8}	1142	1150, ν_{F_8}	1130	1159, ν_{F_8}
ω_6	829, ν_{Br}	816	872, ν_{C1}	790	906, ν_{C1a}
ω_3	621, ν_{Br}	623	648, ν_{Br}	640	667, ν_{C1s}
ω_4	^b 340, δ_{F_8}	340	^a 400, δ_{F_8}	390	^b 455, δ_{F_8}
ω_7	^c 331, δ_{FBr}	330	^a 380, δ_{FBr}	350	437, δ_{FC1s}
ω_9	^b 367, δ_{FBr}	367	440, δ_{FC1}	440	473, δ_{FC1a}
ω_5	^b 282, ν_{Tor}	282	^a 300, ν_{Tor}	260	^b 318, ν_{Tor}
ω_2	^b 165, δ_{Br}	165	^a 200, δ_{Br}	200	^b 261, δ_{C1s}

^a Predicted from combination and overtone bands and related molecules.

^b Raman values.

^c Liquid.

1150, 872, and 648 cm^{-1} . The frequencies ω_4 , ω_7 , ω_5 , and ω_2 were determined from the combination bands, from the calculated frequencies of Stepanov, and from the related molecules CBr₂F₂ and CCl₂F₂.

An examination of the band shapes in the cases of the two symmetric tops, CBrF₃ and CF₃I, further confirms the assignments for these molecules. In both cases the vibrations ω_1 , ω_2 , and ω_3 are of symmetry species A₁, and ω_{68} , ω_{79} , and ω_{25} are of species E. Species A₁ should show a strong central maximum, the transition moment being parallel to the top axis. Species E should lack such a feature and lead to perpendicular bands. A few bands in the spectra of these molecules have envelopes that clearly possess or do not possess a zero branch. In each case this is consistent with the assignments made. For example, in the case of CF₃I, ω_3 at 13.5 μ , and ω_1 at 9.32 μ should and do have central maxima; ω_{68} at 8.44 μ should not and does not have the characteristic P, Q, and R structure.

For the asymmetric tops, this method is not quite as rewarding. For those molecules of point group C_s, CHBrF₂ and CBrClF₂, symmetry considerations show that of the nine fundamental vibrations, three will be of type C (transition moment lying along the axis of greatest moment of inertia), and the remaining six will be hybrids (transition moment having components along the other principal axes of moment of inertia). The type C bands should possess strong central maxima, and the hybrid bands, central maxima of varying prominence. Due to the inability to distinguish the type of band unambiguously, it was felt that consideration of the band envelopes would contribute little.

The remaining molecule, CBr₂F₂, is of point C_{2v}. For this point group, there are three types of bands, A, B, and C, with ω_8 and ω_9 being of the first type, ω_1 , ω_2 , ω_3 , and ω_4 of the second, and ω_6 and ω_7 of the last. Type A and C bands can be expected to show strong central maxima; type B should exhibit central minima. It was possible to check several bands of this molecule, and in every case but one the assignments and band shapes are consistent. Some doubt, however, exists as to the band at 11.43 μ , classified as $\omega_8 - \omega_5$. This is a type C band, but the separation between the P and R branches is great enough to indicate a type A band. If this be a type A band, a possible explanation lies in the spectrum of CBrClF₂. In this spectrum a very strong band of the same shape occurs at the same wavelength. CBr₂F₂, the least pure of the five molecules, may contain CBrClF₂ as an impurity.

4. References

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WASHINGTON, August 14, 1951.